Chemical effects in ion mixing of a ternary system (metal-SiO_2)

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The mixing of Ti, Cr, and Ni thin films with SiO_2 by low-temperature (-196–25 °C) irradiation with 290 keV Xe has been investigated. Comparison of the morphology of the intermixed region and the dose dependences of net metal transport into SiO_2 reveals that long range motion and phase formation probably occur as separate and sequential processes. Kinetic limitations suppress chemical effects in these systems during the initial transport process. Chemical interactions influence the subsequent phase formation.

A number of mechanisms are known to contribute to atomic transport in ion mixing.[1–4] Recoil implantation from single high-energy collisions can be recognized from its linear fluence dependence.[2] A very large number of target atoms experience short range displacements induced by the cascade of higher generation collisions. The motion within a cascade is predominately isotropic, although the anisotropic flux of secondary recoils may also be significant. Electronic interactions introduce chemical effects after the average particle energy has diminished to about 1 eV.[3] Several recent studies have characterized the correlation between the extent of ion-irradiation-induced mixing and thermochemical properties for binary metal-metal systems.[3–5] Much of the mixing in metal-metal systems apparently occurs in this thermalized regime.[6] Chemical effects can bias the random walk motion within this regime and produce a Darken effect. Johnson *et al.* have proposed for these systems that the metallurgical phases are formed after the modified concentration profile is established.[3] Rapid quenching imposes kinetic constraints which may favor formation of metastable phases.

This letter summarizes results from our studies of ion mixing in Ti/SiO_2, Cr/SiO_2, and Ni/SiO_2 bilayers induced by 290 keV Xe irradiation at 25 °C and -196 °C. Thermodynamically, these three systems are quite distinct. There are many favorable reactions of Ti with SiO_2.[7] Segregated $TiSi_2$ and Ti_2O_3 layers were the observed reaction products for thermal annealing above 670 °C. The case of Cr is intermediate; a few of the reactions for Cr forming Cr_2O_3 are favorable but kinetically inhibited.[7,8] The reactions of Ni with SiO_2 are all unfavorable.[7] We compare here the amount of metal transport into the SiO_2 with the morphology of the intermixed region produced by the ion irradiation.

A set of Ti, Cr, and Ni samples on ~ 1 μm thermally grown SiO_2 was prepared by electron beam evaporation with a range of film thicknesses chosen for each metal. 290 keV Xe irradiations were performed at -196° or 25 °C with a prescribed fluence ϕ of 1–15×10^{15} cm^{-2}. The projected range of Xe in these metals is 34 μg/cm^2 with 11.5 μg/cm^2 standard deviation.[9] The unreacted metal was selectively removed after the irradiation by chemical etching, as reported previously.[8,10,11] The distribution of metal in the SiO_2 was measured using 2 MeV He Rutherford backscattering spectrometry (RBS) with a 1–10 mm^2 beam spot. High-resolution cross-sectional transmission electron microscopy (TEM) was used to determine the structure and morphology of the intermixed region. The TEM samples were cleaved and epoxied face to face prior to thinning. X-ray photoelectron spectroscopy (XPS) was employed to identify changes in chemical states. High-resolution cross-sectional TEM images of samples irradiated at 25 °C after removal of the free metal are shown in Fig. 1 for (a) Ti and (b) Cr with

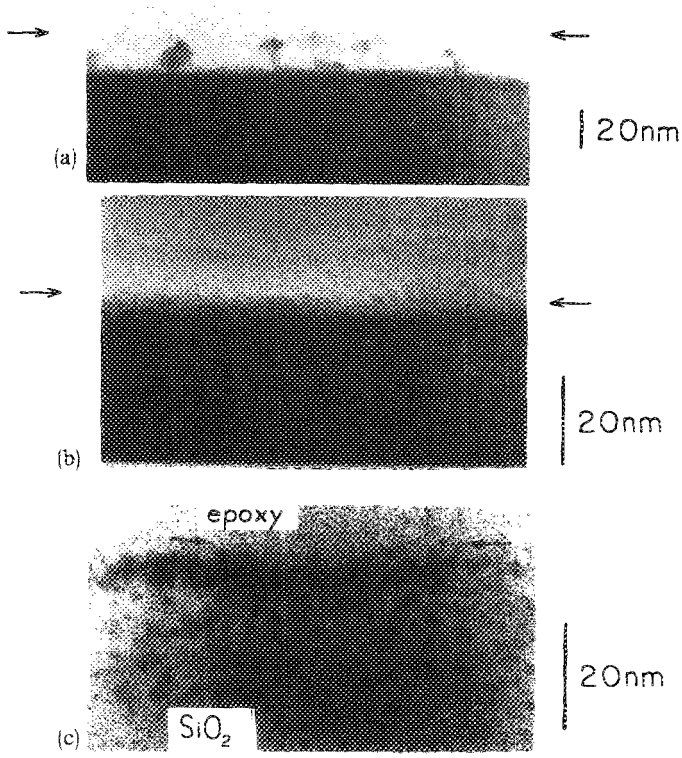

FIG. 1. High-resolution images of irradiated (a) Ti, (b) Cr, and (c) Ni samples after removing free-metal layer.

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$\phi = 10\times10^{15}$ Xe cm^{-2}, and (c) Ni with $\phi = 6\times10^{15}$ Xe cm^{-2}. The initial metal thickness was 23 μg/cm^2. Arrows identify the SiO_2 interface. The dark clusters in (c) correspond to a Ni phase. Most of the apparent Ni is located within a 5-nm region centered 5 nm below the SiO_2 interface. This Ni is contained in crystalline clusters which show a lattice spacing of 0.241 ± 0.004 nm in high-resolution imaging. A single Ni $2p_{3/2}$ line was observed at 853.6 eV binding energy using XPS. These results imply that cubic NiO is the only Ni phase present. The Cr samples show no evidence of crystalline phase formation or clustering. TEM would probably reveal crystalline phases if they were present. TEM is not sensitive, however, to the Cr distribution if it is disordered since the electron scattering factor for Cr is not significantly different from that for Si. The Ti sample in Fig. 1(a) exhibits considerable structure. There are crystalline clusters at the interface which show a lattice spacing of 0.33 ± 0.01 nm. This value corresponds to a strong reflection in several titanium oxides, although it is also possible that they are $TiSi_2$. The Ti $2p_{3/2}$ peak was identified with a 459-eV binding energy, also suggesting oxide formation. There is, in addition, a band of amorphous or partially crystalline material centered at a depth of 10 nm, well beyond the electron escape depth, which probably contains Ti. These results clearly demonstrate that the detailed morphology of the intermixed region is strongly affected by the chemistry of the system.

A different perspective is given by Fig. 2 which shows the RBS average metal concentration $[M]$ plotted logarithmically versus depth x into the SiO_2 for $\phi = 10\times10^{15}$ Xe cm^{-2} at 25 °C. Recall that the depth profile inferred from a RBS spectrum is an average over the area of the sample exposed to the He beam of the actual distribution of atoms in the sample at a depth corresponding to a given energy loss. The profiles in Fig. 2 consist of two distinct parts. Most of the metal is contained in a resolution-limited peak near the interface. In contrast to the Ni bearing region, which clearly lies below the interface, the average distribution of Ti and Cr may extend to the surface monotonically. In each case, a significant discontinuity in the metal distribution is maintained across the metal-SiO_2 interface which is not expected for regular diffusion. The tails extending beyond $\sim$40 nm result from recoil implantation.[8,11] Both the peak and the tail were seen in the RBS spectra for all of the irradiated samples, although with differing proportions. The RBS profiles of samples irradiated at $-$ 196 °C were indistinguishable from the 25 °C samples.

The areal density of M atoms incorporated in the SiO_2, $[M]_s(\phi) = \int[M](\phi,x)dx$, can be calculated from the profiles such as shown in Fig. 2 for different doses ϕ. It is found for each sample configuration that $[M]_s \simeq \alpha_M\phi^1 + \omega_M\phi^{1/2}$. This was deduced from a linear relationship observed between $\phi^{-1/2}[M]_s$ and $\phi^{1/2}$ over the investigated fluence range. The ϕ^1 component arises from anisotropic processes while random walks generated by overlapping cascades introduce a $\phi^{1/2}$ dependence. For a given initial film areal density, the α_M are similar among Ti, Cr, and Ni. This is expected if recoil implantation is the dominant anisotropic process since these metals are collisionally similar. The mixing associated with ω_M correlates linearly with the energy deposited in the metal per incident Xe per unit depth (F_D) at the interface.[8] There is, however, no grouping of the data points to suggest a chemical trend.

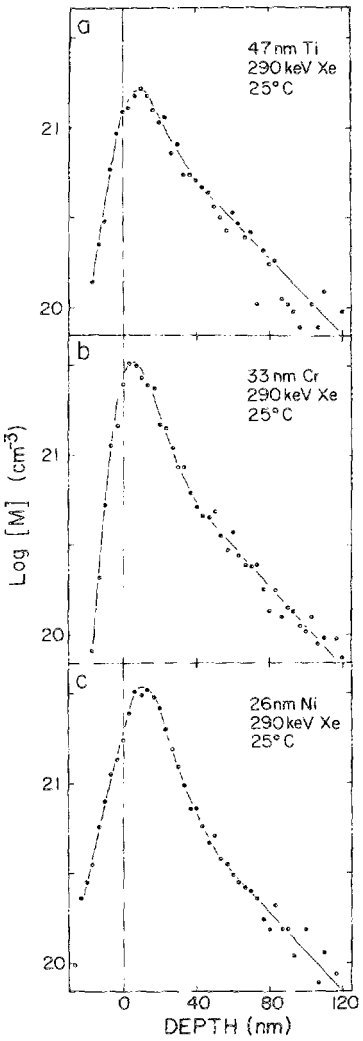

FIG. 2. RBS depth profiles of (a) Ti, (b) Cr, and (c) Ni in SiO_2 produced by 10×10^{15} cm^{-2} Xe irradiation. The free metal was previously removed.

Over the dose range investigated, the number of metal atoms incorporated in the SiO_2 follows the same description for all three metals. We conclude from this common behavior that in this dose range the process responsible for the metal incorporation into the SiO_2 is probably the same for all three metals, even though the individual chemistry of these metals with SiO_2 is different. This contrasts with the mixing behavior of transition metal bilayers, where the ion mixing at low temperatures (i.e., in the absence of radiation enhancements) correlates with chemical mixing enthalpies.[3,4] The different chemical affinities are expressed in the final morphology (Fig. 1), not in the average spatial distribution of the metal in SiO_2 (Fig. 2) or its dose dependence. The dominant processes governing mixing in Ni/SiO_2 were tentatively identified by a series of parametric investigations.[8] For $\phi > \sim 10^{15}$ cm^{-2}, the concentration of Ni near the interface is probably determined by the competition between second-

ary recoil injection of Ni into the SiO_2 and difffusion of Ni back to the Ni-SiO_2 interface. The injection could have a linear F_D dependence.[8,12]

Our observations only partly concur with other reports. Farlow *et al.*[13] find little mixing for Cr on SiO_2 under experimental conditions similar to ours, but report substantial mixing for Ti on SiO_2. In contrast, we observe similar mixing for both Cr and Ti at room temperature and below. The reasons for this discrepancy are unclear.

Additional discrepancies arise when comparing published results for Cr at elevated temperatures. Farlow *et al.*[13] see a decrease in the mixing of Cr on SiO_2, while earlier work reports the opposite.[10] Nickel intermixes less at elevated temperatures than at room temperature, while the converse is true for Ti.[10] This is readily understood as an expression of the chemical driving force in the system when kinetic limitations disappear.[13] In the case of Cr, the chemical driving forces are weak and the outcome may be dominated by second-order effects. This is suggested by the apparent discrepancy in the mixing of Cr at elevated temperatures.

The results reported here for Ti, Cr, and Ni show that at room temperature kinetic constraints impede the influence of chemical driving forces. White *et al.*[14] show that Nb mixes more readily with SiO_2 at room temperature than Ti, Cr, and Ni do. In the Nb case, the kinetic constraints are evidently relaxed. We believe that the kinetic constraints are associated with the evolution of a cascade. A dense cascade can last long enough to allow for significant chemical interaction.

In summary, it is found that at room temperature and below, the net transportation of metal into the SiO_2 is similar for Ti, Cr, and Ni. For these systems, the amount of intermixing does not correlate with the metal's reactivity. This suggests that there are kinetic limitations associated with a high activation energy for the relatively complicated exchange reactions, as occurring in these ternary systems, and the short duration of the cascade. At low temperatures, the metal depth distribution is probably established before chemistry is important. The limitations can be circumvented at elevated irradiation temperatures where the mixing rate shows a positive correlation with reactivity.[10]

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